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A cationic polymer enhanced PAC for the removal of dissolved aquatic organic carbon and organic nitrogen from surface waters

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ABSTRACT:

Dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) are important components of the aquatic environment and may produce harmful disinfection by-products through chlorination associated with water treatment processes. Therefore, it is necessary to remove them from the water. Coagulation is a cost-effective water treatment technique as the key unit in the pretreatment of drinking water but deals poorly with DON. We present a study to investigate the enhancement of poly aluminum chloride (PAC) using a cationic polymer for the removal of both DON and DOC. The cationic dimethyl diallyl ammonium chloride (PDMDAAC) polymer was hybridised with PAC to remove DON and DOC. The results showed that the PDMDAAC increased the charge neutralization capacity of PAC and floc aggregation thereby increasing the settling efficiency of flocs; the PDMDAAC increased the amount of colloidal species in PAC, which was beneficial to the formation of adsorption-bridging; with the increase

of pH, a greater proportion of colloidal adsorption sites were used in the removal of DON; the DOC, DON and turbidity removal were dependent on multiple interactions through charge neutralization, adsorption-bridging and floc sweeping. However, DOC and DON removal were primarily determined by adsorption-bridging and floc sweeping, while turbidity removal was mainly dependent on charge neutralization.

KEYWORDS: coagulation; dissolved organic nitrogen; dissolved organic carbon; Al-based coagulation; cationic polymer

INTRODUCTION

Dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) are important components of dissolved organic matter (DOM) in aquatic environments[1], soil environments [2] and other parts of surface environments[3; 4]. The DOC and DON are two different types of organic compounds because DOC is made up of the hydrophobic fraction and high molar mass compounds but the DON is characterized by small high molar mass compounds and hydrophilic fractions [5]. The DOC accounts for large portion of DOM while DON only comprises a small portion of DOM in surface water (about 0.5–10% by weight) [6]. Whilst DOC has been widely studied, the academic community has only more recently shifted its focus to DON because of its role in generating harmful nitrogen-based disinfection byproducts (N-DBPs), which have both reproductive toxicity and carcinogenicity[7]. For example, DON has been identified as providing most of the precursors needed to form N-nitrosodimethylamine (NDMA) [8], thus contributing much to NDMA formation [9]. Also, NDMA has been found to have a higher concentration than other nitrosamines in drinking water [10]. Therefore, reducing NDMA concentration is essential to the health of the world's population. The technology to control the content of the precursors will

play a key role in lowering the content of disinfection byproducts. DON has also caused other environmental issues such as membrane fouling [11] and eutrophication [12]. Overall, to keep water sources clean and quality reliable, we need to identify technologies that can treat contaminated water and prevent further DON pollution.

Many methods have been used to treat DON pollution, these include examples of physical, chemical and biological treatment processes [13]. Physical treatment includes adsorption [14] and membrane filtration [15]. Chemical treatment includes an advanced oxidation process [16]. Researchers have tackled this problem with biological treatment, such as anaerobic microbial digestion [17], use of algae [18; 19], biological filtration [20], and fixation within artificial wetland [21]. For high quality potable water purification, adsorption materials are difficult to recycle. Membrane fouling and operational costs need to be addressed. The advanced oxidation process is expensive. Thus far, only hydrophilic DON has been effective for bioavailability reduction [22; 23] and the release of microbial products has possibly led to an increase in the levels of DON. From the present treatment methods for DON removal from water and waste water, the treatment cost and efficiencies are the core issues, thus for those plants using conventional water treatment processes, the cost-effective and convenient treatment methods are the urgent requirement. Coagulation is the most un-expensive process, which has long been the core unit in drinking water plants. Effective coagulation has been beneficial to post-treatment processes, and has improved water purification efficiency.

Unfortunately, the coagulation methods currently applied are not always effective for DON removal. Compared to activated carbon, biological aerated filters and sand filters, coagulation has

not been as effective in DON removal [24-25], but is often effective for the hydrophobic fractions. However, DON consists predominantly of hydrophilic fractions. A previous study showed that in a wastewater treatment plant effluents, hydrophilic fractions in DON made up as much as 80% of the water needing purification [22]. Effective DON removal by coagulation is lower when this happens, with an average DON removal efficiency of only 20% found in 28 water treatment plants in a study in the USA [24]. However, when the water samples included higher molecular weight compounds, DOC has a larger removal efficiency and enhanced coagulation is not effective for DON [27]. The recommended coupling processes are potassium permanganate/coagulation [28], coagulation/adsorption [29], and ozone/coagulation [30]. It appears that single coagulation is difficult to use for effective DON treatment.

Therefore it is critical that research focuses on the development of coagulants that can better remove DON. In colloidal solutions, colloidal particles and coagulants have a wide variety of physical and chemical species, and these are important factors that determine the nature of the coagulation processes and its efficiency [31]. In the coagulation process, the coagulant species vary on the basis of a range of characteristics. Varieties include aluminum, iron or hybrid inorganic-organic coagulant function can be identified through a significant positive correlation with the removal of pollutants such as DOC, UV254 and turbidity. Although previous research has indicated that all types of coagulant species have affected DON removal [5], their transformation and interaction in different aquatic systems, and their correlation with DON removal has not been addressed. Low removal of DON in the coagulation process has shown that the development of coagulant species should be given more attention. Application of cationic polymers enhances DON removal for inorganic coagulation but the mechanisms still need to be discussed [32; 33].

The coupling of aluminum sulfate coagulant and cationic poly dimethyl diallyl ammonium chloride (PDMDAAC) could enhance the removal efficiency of DON but the absolute removal will still not be high [32]. The selection of a coagulant type with an appropriate chemical species has to date been missed [32]. The response of hydrophobic compounds are different from those of the hydrophilic organic compounds during treatment, however, very few reports focus on the flocculation differences between DON and DOC [26, 5]. Research on the effect of coagulant species and their role in the water environment towards more effectively removing pollutants needs to focus on identifying the removal mechanisms between DON and DOC, with major advantages in improving the safety of drinking water.

In this study, evaluation of the enhanced polymeric aluminum chloride (PAC) coagulation for DON and DOC by cationic PDMDAAC was assessed as well as the coagulation differences between the two contaminants. The study focused on employing reasons for enhanced coagulation and mechanisms. The hybrid coagulant of PAC and PDMDAAC was prepared and labeled as PAC-PDMDAAC. The variations of coagulant species in the presence/absence of PDMDAAC as well as in the coagulation process was investigated. In addition, floc aggregation and zeta potential analyses were also used to further the advancement of enhanced coagulation mechanisms.

2 MATERIALS AND METHODS

2.1 Materials

All reagents used in this study were of analytical grade and included reagents such as aluminum

chloride (Tianjing Stellar Reagent Co., Ltd., China), sodium acetate (Sinopharm Chemical Reagent Beijing Co., Ltd., China), hydrochloric acid (Zhuzhou XingKong Huabo Co., Ltd., China), sodium carbonate (Tianjin Institute of Chemical Reagents, China), phosphoric acid (Hunan Huihong Reagent Co., Ltd., China), phenanthroline (Tianjin Kermel Chemical Reagent Co., Ltd., China), hydroxylamine hydrochloride(Tianjin Fengchuan Chemical Reagent Technology Co., Ltd., China), and ferron (8-hydroxy-7-iodoquinoline-5-sulfonic acid) (Sinopharm Chemical Reagent Beijing Co., Ltd.,China). Commercial PDMDAAC (molecular weight is one hundred thousand) with a 40% cationic degree was purchased (Zouping Mingxing Chemical Co. Ltd., Binzhou, China). A commercial humic acid was purchased from Aladdin Industrial Corporation. All aqueous solutions were prepared with ultrapure water using an ultrapure LBY-20 water purifier (Chongqing OWEN Science and Technology Co. Ltd.). The glassware and other labware were acid-washed, rinsed thoroughly with deionized water, and dried prior to use.

2.2 Coagulant preparation and characterization

Liquid coagulants were prepared in a water bath at a constant temperature of 90 °C. First, 72.45 g of aluminum chloride hexahydrate were dissolved with 75 mL of distilled water. Concentrated phosphoric acid was subsequently added into the above solution with a predetermined molar ratio of $n_P/n_{Al} = 0.3$. After a reaction for 2 hours under a water bath at 90 °C with a stirring speed of 300 rpm/min, the sodium carbonate was then added with a predetermined molar ratio of $n_{OH}/n_{Al} = 0.09$. After a reaction for 1 hour, a predetermined volume (6 mL) of PDMDAAC was then added. The reaction solution continued to stir for 12 hours at a rapid speed of 1000 r/min at a room temperature. Finally, a homogeneous liquid was generated, which was the hybrid coagulant

141 referred to as PAC-PDMDAAC. After at least 24 hours of aging, the coagulant could be used for
142 water treatment. Without PDMDAAC, the prepared coagulant was an enhanced polymeric
143 aluminum chloride (PAC). The Al_2O_3 mass percent in PAC and the hybrid coagulant were
144 measured with an acid-base titration according to Chinese Standard GB 15892-2009. The results
145 showed the Al_2O_3 mass percent of 11.24% in PAC-PDMDAAC and 13.48% in PAC, which met
146 the requirement of Chinese Standard GB 15892-2009.
147
148 ***2.3 Water samples and coagulation test***
149 Water samples collected for coagulation included artificial lake water, river water, wetland water,
150 wastewater plant effluent, artificial pool water, natural pool water, algal solution. The
151 characteristic parameters of the water samples are shown in Table 1. Artificial lake was located on
152 the Hunan University of Science and Technology campus. Other water samples were collected
153 around the campus except for algae suspension (Microcystis aeruginosa). Algae solution was
154 prepared in the laboratory.
155
156 **Table 1** Characteristic parameters of water samples.

Water Type	**pH**	**Turbidity (NTU)**	**UV254 (cm^{-1})**	**DOC (mg/L)**	**DON (mg/L)**
Upstream River water	7.5	11.43	0.04	15.62	0.75
Downstream River water	7.7	9.52	0.03	15.11	0.73
Wetland water	7.4	7.67	0.08	21.95	0.81
Wastewater plant effluent	7.1	3.31	0.04	25.07	1.08
Artificial Pool water	8.6	32.40	0.12	23.29	0.77

Natural pool water	7.4	8.02	0.05	19.48	0.60
Algae solution	7.3	3.01	0.03	27.40	0.97
Artificial lake water	7.0–8.0	8–15	< 1.0	8–16	< 1.0

Coagulation experiment was performed using a program-controlled jar test apparatus (ZR4-6, ZhongRun Water Industry Technology Development Co. Ltd., Shenzhen, China) at room temperature. One liter of each water sample was transferred into a beaker and the initial pH of the sample was adjusted to the set value using 0.5 mol/L HCl and 0.5 mol/L NaOH. The sample was rapidly mixed at the set agitation speed (rpm) for 2 min, followed by a slow mixing phase at 70 rpm for 15 min, and then a 30-min settling time. The supernatant sample was extracted from the beaker 2 cm below the water surface to measure water quality parameters. The concentration of coagulant added to the water sample was calculated using the quantity of Al_2O_3 component.

2.4 Analytical method

Turbidity and DOC were measured using a 2100Q Portable Turbidimeter (HACH, USA) and the vario MICRO Cube (Elementar Analysensysteme GmbH, Germany), respectively. DON was measured using a K9840 Kjeldahl apparatus (Hanon Co. Ltd., China). UV254 was measured using a TU-1910 UV–Vis spectrophotometer (Beijing Puxi General Instrument Co., Ltd., Beijing, China). The neutralization capacity of coagulant was assessed by measuring the zeta potential value (ζ) using a Zetasizer Nano S90 (Malvern Instruments, Malvern, UK). When coagulant was added to the water sample, the ζ value was immediately measured. Water samples were analyzed after the samples were filtered through a membrane (pore size = 0.45μm) except for turbidity and ζ values.

Fluorescence spectra of water samples that were filtered with a membrane filter (ore size=0.45 μm) was tested using a fluorescence spectrophotometer (FL4600, Hitachi High Technologies, Tokyo, Japan). The fluorescence intensity of an ultra-pure water as a blank sample was subtracted from water samples. The Rayleigh and Raman scatter were removed according to the method shown in reference [34]. Fluorescence region integration (FRI) developed by Chen, et al.[35], divided two-dimensional fluorescence excitation region into five parts including aromatic protein-like materials denoted as I, aromatic protein-like materials denoted as II, fulvic acid-like materials denoted as III, soluble microbial metabolites denoted as IV, humic substance-like denoted as V. The integral volume of each of the above fluorescence regions is calculated as ϕ which reflects the relative content of organic matter in the integral region. Their reduction rates are determined by the subtraction of each part between that before coagulation and that after coagulation. The integral volume value is expressed as follows.

$$\phi_{i,n} = \alpha_i \int_{ex} \int_{em} I d\lambda_{ex} d\lambda_{em} \quad (1)$$

where $\phi_{i,n}$ (au.nm^2) is standard integral volume of i^{th} fluorescence region; λ_{ex} is the excitation wavelength (nm); λ_{em} is the emission wavelength (nm) ; I is fluorescence intensity value at corresponding to λ_{ex} and λ_{em} ; α_i is the ratio of the integral volume of all regions and the integral volume for the i^{th} region.

A ferron-complexation timed spectrophotometric method denoted as the ferron method was used to investigate the species of coagulant in a solution based on the standard adsorption curves of the reaction between PAC, PAC-PDMDAAC and the ferron reagent. The ferron reagent was rapidly prepared: 0.5 g 8-hydroxy-7-iodoquinoline-5-sulphonic acid and 0.025 g phenanthroline were

dissolved and diluted to 250 mL in a volumetric flask; 10 g hydroxylamine hydrochloride and 4 mL of 6 mol/L HCl were dissolved and diluted to 100 mL in a volumetric flask; 58.04 g of sodium acetate trihydrate were dissolved and diluted to 100 mL. The above three kinds of solutions were mixed and diluted to 500 mL in a volumetric flask; finally, the pH of solution was adjusted to pH 5 approximately. A preliminary test was conducted to investigate if the complex reaction of the coagulant and ferron reagent could form a color complex. Both PAC-PDMDAAC and PAC can react with the ferron reagent forming a color complex at the same characteristic peak of $\lambda = 362$ nm. The absorbance of the color complex solution in the presence of sodium acetate solution (35%, m/m) at pH 5 was linear to Al concentration with a squared correlation coefficient of 0.9996 in the Al range of 10^{-5} to 10^{-4} mol/L. The visible light absorbance was measured as a function of time at $\lambda = 362$ nm to quantify the amount of hydrolytic species. Those species reacting with the ferron reagent within 1 min were monomeric species, denoted as Al_a. Those species reacting to the ferron reagent during the next 4 hrs were medium polymeric species, denoted as Al_b. The results of a preliminary test determined that absorbance did not increase after monitored for 4 hrs; therefore, any species that remained unreacted after 4 hrs was a colloidal species, denoted as Al_c. The total Al concentration was measured using the colorimetry method [36]. Prior to the measurement, the sample was acidified to pH < 2 with concentrated nitric acid. The total Al species content was denoted as A_T. With the contents of Al_a and Al_b species, the content of Al_c species was calculated by the following equation.

$$Al_c = Al_T - (Al_a + Al_b) \quad (2)$$

The reduction rate of species concentration was defined as follows.

$$q = \frac{C_0 - C_e}{C_0} \text{ x } 100\% \quad (3)$$

where q is the removal efficiency; C_0 and C_e are the initial concentration and final concentration measured after coagulation, respectively.

Dynamic floc size was monitored using a Malvern Mastersizer 2000 laser diffraction instrument (Malvern, UK) during floc formation, breakage and reformation. The median volumetric diameter (d_{50}) was denoted as floc size. Three parameters were used to assess the floc growth characteristics, floc growth rate (G_r), a strength factor (S_f) and a recovery factor (R_f) [37]. The given G_r, S_f and R_f equations are as follows.

$$G_r = \frac{\Delta size}{\Delta time} \quad (4)$$

$$S_f = \frac{d2}{d1} \quad (5)$$

$$R_f = \frac{d3 - d2}{d1 - d2} \quad (6)$$

where $\triangle_{size}$ is the difference between minimum and maximum of median flocs size in the rapid growth region of flocs, which corresponds to a time duration for rapid growth, $\triangle_{time}$; d_1 is the average median floc size of the steady phase before breakage; d_2 is the median floc size after it was subjected to high shear rate; the average median size, d_3, is the average median floc size of

248 the steady phase of flocs after floc breakage.

249

250 **3. RESULTS and DISCUSSION**

251 ***3.1 The comparison between PAC and PAC-PDMDAAC***

252 After assessing the effect of coagulants on the removal of artificial lake water turbidity, the DOC
253 and DON was investigated with the initial water pH at 7.0 in this study. The initial turbidity, DOC
254 and DON concentration was 8.35 NTU, 10.02 mg/L and 0.76 mg/L, respectively.

255

256 PAC had a lower performance in the settling speed of colloids and in the removal efficiencies of
257 DON and DOC than PAC-PDMDAAC. Although the amount of residual turbidity with PAC-
258 PDMDAAC was close to that with PAC after settling 30 min (as shown in Figure 1a), the
259 turbidity reduction after settling before the first 15 mins at 6 cm below the surface of suspension
260 went faster, showing a stronger settling speed with PAC-PDMDAAC (Figure 1b). The PAC-
261 PDMDAAC had a better effect on DOC and DON removals than PAC (Figs. 1c and d) below 30
262 mg/L. The overdosing effect showed that coagulants can play an adsorption-bridging role
263 between particles surfaces only when the coagulant concentration is sufficiently small compared
264 with the amount of saturated adsorption points [38; 39]. With the excess dose, resulted in a
265 deterioration of water quality as well as turbidity. Thus, DOC and DON removal efficiencies were
266 decreased with PAC-PDMDAAC. This showed that adsorption-bridging is an important
267 coagulation mechanism of PAC-PDMDAAC. The PAC-PDMDAAC achieved a better effect on
268 the removal of DOC and DON with a lower dose than PAC (Figure 1c). However, DON removal
269 behavior did not follow the DOC removal pattern. Hence, a lower coagulant dose was needed for
270 the DON removal than that for the DOC removal (Figure 1d).

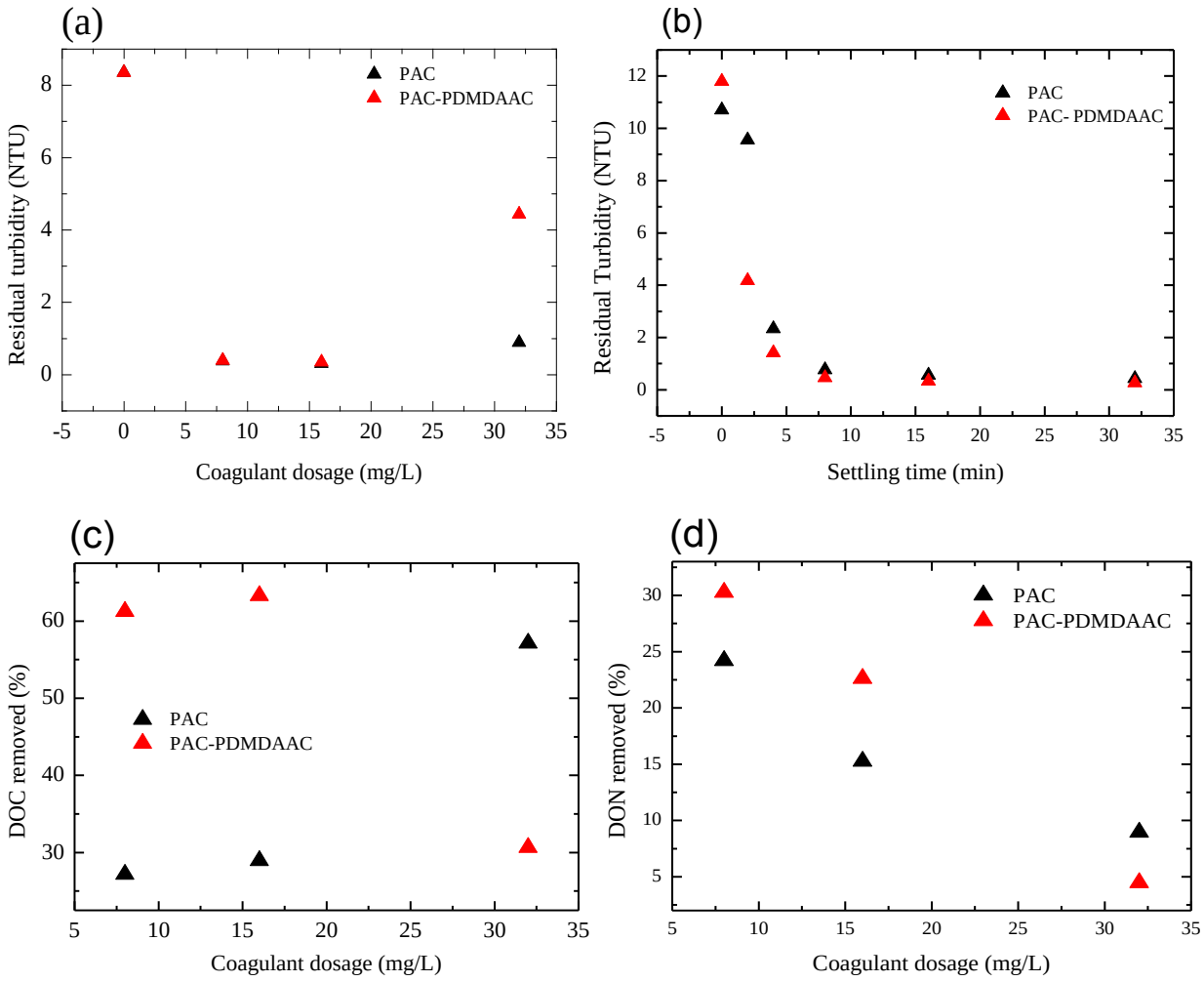


Figure 1 A comparison between PAC-PDMDAAC in: (a) turbidity removal which was recorded after 30 min settling, (b) settling speed with coagulant dose of 20 mg/L, (c) DOC removal which was recorded after 30 min settling, and (d) DON removal which was recorded after 30 min settling.

3.2 Coagulant dose effect

The effect of coagulant dose in the range of 5 mg/L to 30 mg/L on the removals of DON, DOC and turbidity was examined in this study using PAC-PDMDAAC. The initial artificial lake water pH was 7.0. The initial turbidity of DOC and DON were 14.3 NTU, 14.4 mg/L and 0.61 mg/L,

respectively. The experimental results which were recorded after 30 min settling are shown in Figure 2.

As seen from Figure 2a, the DOC removal followed the same trend as in the case of turbidity reduction. At a coagulant dose of 20 mg/L, the DOC and turbidity removals achieved the maximum removal rate of 65.3% and 98.3%, respectively. However, the turbidity removal was different from DOC removal, its removal efficiency achieved the approximate maximum, 98.1%, with a lower coagulant dose of 10 mg/L. The coagulant dose of 20 mg/L for DOC removal efficiency could only be achieved at the maximum 65.3% turbidity removal rate. With the coagulant dose increased from 5 mg/L to 20 mg/L, both turbidity and DOC removal increased but with an excess of 20 mg/L, they both decreased. The main reason for the reduction was also attributed to the overdosing effect. DON removal had a different characteristic from DOC and turbidity removal efficiencies (Figure 2b). With the increase of coagulant dose over the range investigated, the DON removal decreased. For a better removal of DON, a lower dose was required compared to that for the enhanced removal of DOC and reduction in turbidity.

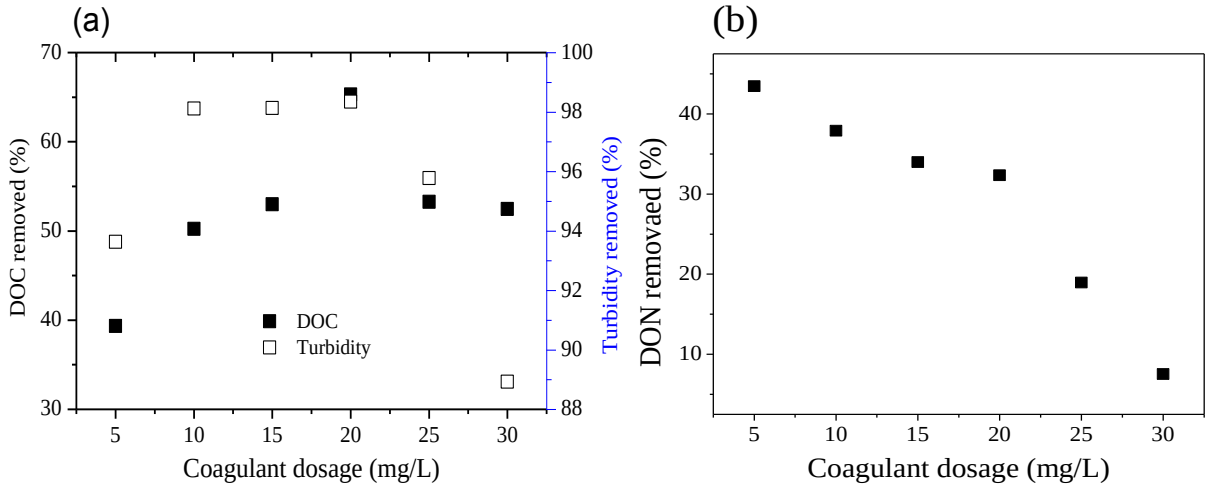


Figure 2 (a) Coagulant dose effect on turbidity and DOC removal and (b) DON and DOC removals.

3.3 pH effect

The effect of initial artificial lake water pH in the range of 4 to 9 on the removals of DON, DOC and turbidity was investigated in this study using PAC-PDMDAAC. The coagulant dose of 20 mg/L was used. The initial turbidity, DOC, and DON were 10.7 NTU, 15.3 mg/L and 0.52 mg/L, respectively. Experimental results which were recorded after 30 min settling are presented in Figure 3.

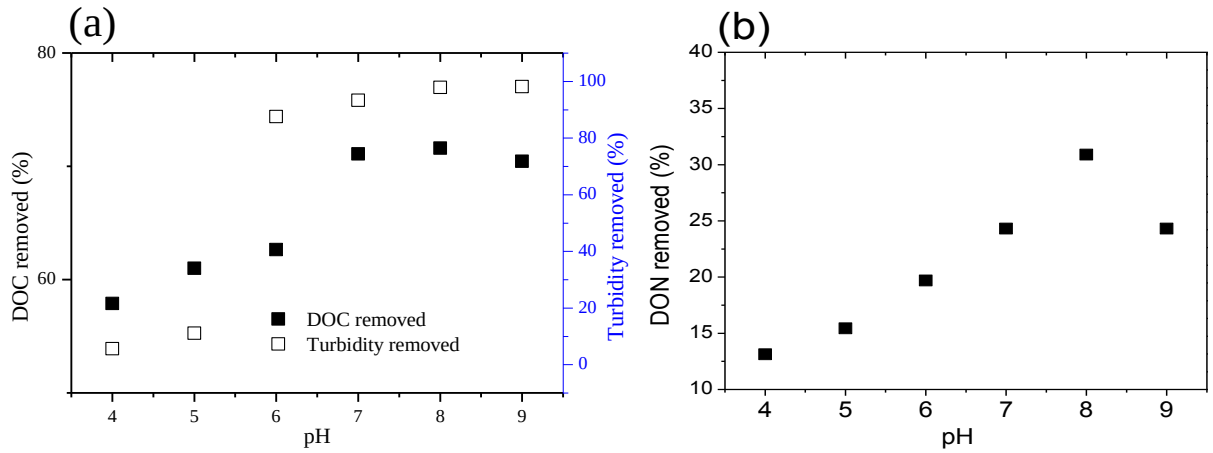


Figure 3 Effect of initial artificial lake water pH on (a) turbidity reduction and DOC removal and (b) on DON and DOC removal.

As seen from Figure 3a, the reduction in turbidity increased with the increase of pH. At pH 4 and 5, the turbidity reduction was less than 20%. The turbidity reduction increased to 87.6 % at pH 6 and at a higher pH, the turbidity reduction efficiency still increased. At pH 8 it achieved the approximate maximum, 97.9%. The maximum removal efficiency, 98.13%, was achieved at pH 9. DON and DOC removal efficiencies achieved the maximum at pH 8 (see Figures 3a and b), but low efficiencies occurred at pH 4 to 5. Both removal efficiencies of DON and DOC increased

with the increase of a pH below 8 because more amorphous $Al(OH)_3$ formed to remove organic matter by adsorption during the precipitation of Al hydroxide flocs via flocs sweeping mechanism [40]. At pH 9, more negatively charged $Al(OH)_3$ flocs or $Al(OH)_4^-$ ions formed, and the organic matter did not easily adsorb onto $Al(OH)_3$ flocs or $Al(OH)_4-$ due to the increased electrostatic repulsive force among colloids; resulting in decreased DON and DOC removal. Overall, the alkaline conditions were more suitable for reduction in turbidity.

3.4 The enhanced floc aggregation

The PAC, in the presence of PDMDAAC, provided better settling ability. The enhanced settling performance was related to the cationic polymer effect on enhancing floc formation. Figure 4 shows the characteristics of floc formation. In the test, the PAC and PAC-PDMDAAC coagulant dose were 20 mg/L. The sample tested in this study was artificial lake with pH at 8.32. The PAC-PDMDAAC had a faster aggregation and settling performance as well as regrowth capacity. With PAC and PAC-PDMDAAC, floc formation processes were different. With PAC-PDMDAAC, the median floc size was significantly larger than that with PAC in the steady phase, and it had a larger the G_r value of 154.99 μm/min, while with PAC, the G_r value was 79.01 μm/min. The stronger G_r value implies that PAC-PDMDAAC gave a faster aggregation and had a better adsorption bridging performance [41]. PAC-PDMDAAC had a larger recovery factor of 16.27% than that of R_f = 9.49% with PAC, which showed flocs have a better recovery capacity after breakage. Floc strength was related to the number and strength of inter-particle bonds within flocs, while the smaller flocs were more compact [41; 42]. In the presence of larger floc sizes, a lower resisting shear force accompanied PAC-PDMDAAC. The resistance of flocs to stress in the presence of PDMDAAC was, therefore, possibly decreased. The strong factor of 34.67% tested in

this study was slightly lower than that of PAC at S_f = 38.86%. Overall, the above results showed an effective hybrid effect in enhancing floc aggregation that possibly improves settling performance.

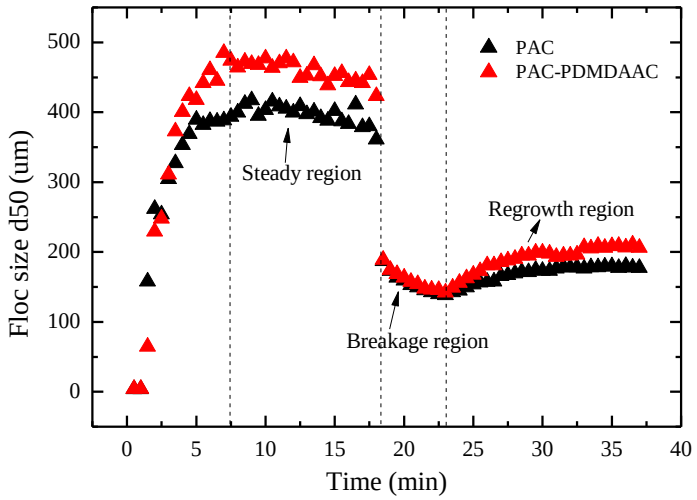


Figure 4 The growth, breakage and regrowth profiles of flocs with time.

3.5 The enhanced charge neutralization capacity

The presence of cationic PDMDAAC could increase the charge neutralization capacity of PAC by assessing ζ. With PAC and PAC-PDMDAAC, the ζ value was measured in the coagulation of artificial lake water at an initial pH of 7.8. The initial water ζ value was −10 mV. The results are presented in Figure 5a. Throughout the whole investigated dose of 4 mg/L to 16 mg/L, with PAC-PDMDAAC the ζ values were all higher than that with PAC. This indicates that the PDMDAAC could help PAC improve charge neutralization capacity. The charge neutralization capacity was also investigated through the pH effect on the ζ value with a coagulant dose at 20 mg/L as shown in Figure 6b. It showed that PAC and PDMDAAC increased the ζ value with PAC at the same tested pH, which was less than 7.0. The ζ value with PAC-PDMDAAC decreased with the pH,

but it almost increased in a wide pH range (from 4.0 to 7.0). The main reason for ζ reduction from pH 8 was attributed to the increase of negatively charged complexes of coagulants and organic matter. The PDMDAAC, therefore, enhanced the neutralization capacity of PAC.

Zero potential appeared between 8 mg/L and 12 mg/L for PAC and PDMDAAC with a pH between 5 and 6 for PAC. Better removal efficiencies of DOC and DON with PAC or PAC-PDMDAAC did not appear at the near zero potential where charge neutralization was mostly effective for removal of pollutants. Therefore, the dominant mechanism for the removal of organic matter was not charge neutralization. On the contrary, efficient turbidity reduction appeared around a zero potential at a coagulant dose of around 10 mg/L as seen from Figs. 5a; thus, it showed its removal was dependent on charge neutralization. For a common coagulation by charge neutralization, the effective pH range was found to be between 4.0 and 5.5 [43]. At pH 6, most of turbidity could be removed with PAC-PDMDAAC with $\zeta < 7$ mV (see Figure 3a and 5b). With less coagulant dose, the ζ could be reduced to around zero potential point, and the turbidity removal would be better. Therefore, it would reduce the amount of coagulant dose used in water treatment. Under alkaline conditions, the PAC-PDMDAAC was also effective for turbidity removal with a relatively higher removal value than that at pH 6, which implies that floc sweeping aids the charge neutralization to improve turbidity removal.

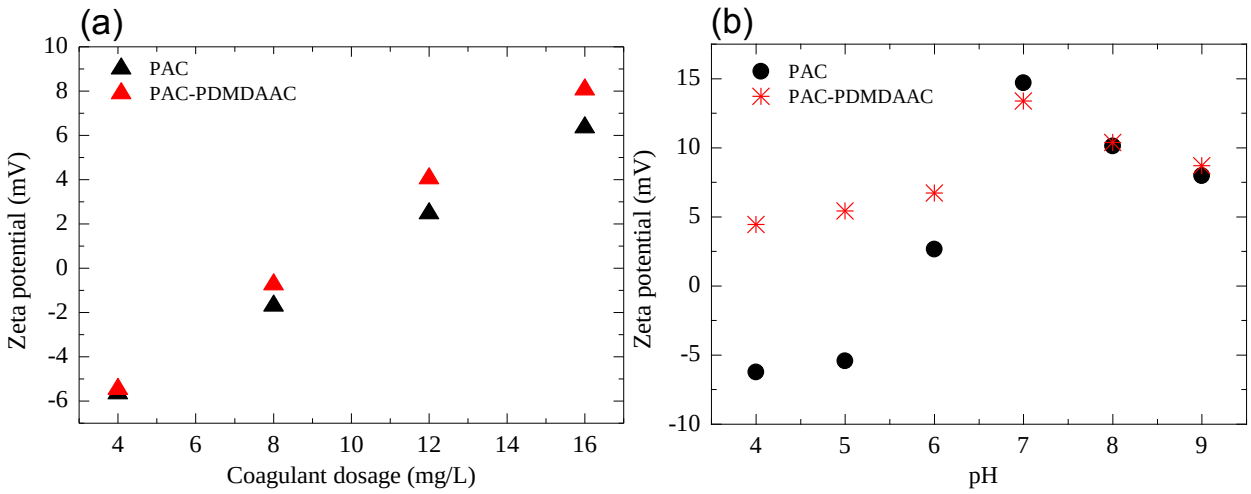


Figure 5 Zeta potential by varying (a) coagulant dose and (b) pH at coagulant dose of 20 mg/L.

3.6 The enhanced colloidal species

The PAC-PDMDAAC had higher proportion of colloidal species. The colloidal species increased with the increase of PDMDAAC as shown in Figure 6a. The PAC-PDMDAAC included n_P/n_{Al}, n_{OH}/n_{Al} = of 0.3, 0.12, respectively. The dose of PDMDAAC used was from 0 mg/L to 10 mg/L. The results showed that both monomeric species and medium polymeric species decreased with the increased proportion of colloidal species. The increase of colloidal species was conducive to adsorption bridging of organic matter. As shown in Table 2. The colloidal species in PAC-PDMDAAC found in this study was the highest, greater than that in PAC. The study of PAC showed the highest proportion of medium species, which was higher than that in PAC-PDMDAAC. Because the amount of monomeric species and medium species in PAC was both higher than that in PAC-PDMDAAC, in the presence of PDMDAAC, the medium species and monomeric species in PAC were transformed to colloidal species.

The influence of three kinds of species on removals of DON, DOC, and turbidity was different. Medium species are considered capable of performing a dominant adsorption-bridging function in

the removal of DOM (e.g., DOC and UV_{254}), followed by the colloidal species and the monomeric species [44; 45]. Other research [45] has shown that the colloidal species play the dominant role in adsorption-bridging of DOC and UV_{254}, followed by the medium species and monomeric species [46]. Therefore, the dominant species task of removing organic matter appears to differ. In this study, it was shown that the colloidal species played the dominant role in removing DON and DOC, followed by medium species and monomeric species. The decrease in the level of medium species and monomeric species possibly decreased the charge neutralization capacity of PAC-PDMDAAC. However, the real charge neutralization capacity increased. This was attributed to the presence of the positive charge of cationic polymer. Therefore, the increase of colloidal species didn't affect the charge neutralization capacity of PAC-PDMDAAC.

There was a higher reduction rate in colloidal species of PAC-PDMDAAC than in that of PAC in the coagulation process. Figure 6b shows the species reduction rates with a coagulant dose of 8 mg/L and 16 mg/L. Compared to PAC, PAC-PDMDAAC was largely reduced in the proportion of colloidal species (Figure 6b) with the same dose. It had a stronger adsorption bridging of organic matter because it had higher efficiency in removing DON and DOC than PAC. The monomeric species and medium polymeric species in both PAC and PAC-PDMDAAC also had a higher reduction of over 90%. Therefore, pollutant removal should be the result of multiple coagulation mechanisms.

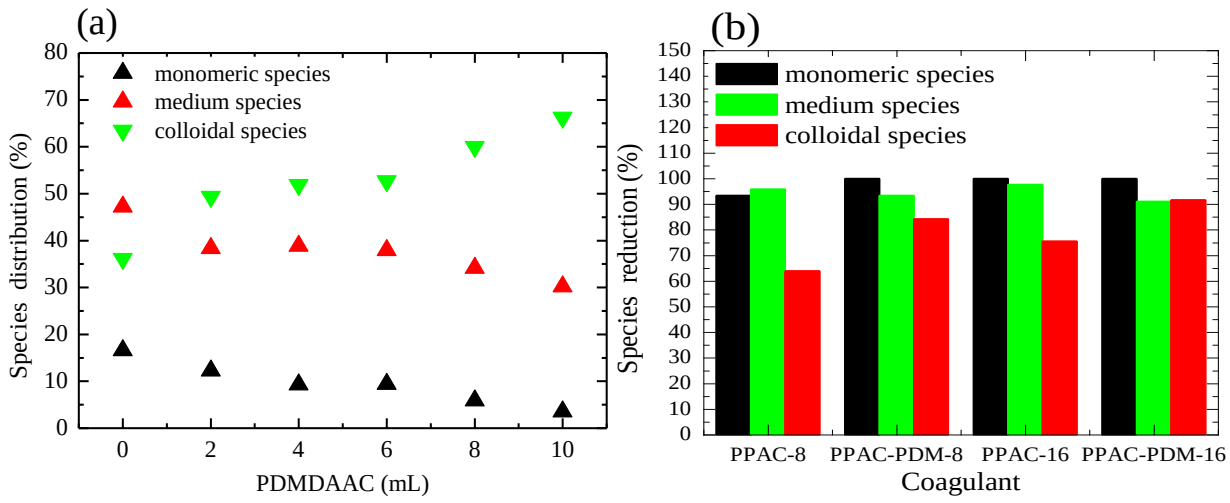


Figure 6 (a) Influence of PDMDAAC dose on species distribution and (b) species reduction by PAC and PAC-PDMDAAC at 8 mg/L and 16 mg/L, respectively.

Table 2 Species distributions under different pH conditions.

	Monomeric species (%)	Medium species (%)	Colloidal species (%)	Monomeric species (%)	Medium species (%)	Colloidal species (%)
4	24.89	47.50	27.84	13.95	38.21	47.83
5	15.33	57.45	26.77	12.82	38.42	48.76
6	14.66	61.29	23.57	10.09	37.54	52.37
7	13.49	66.51	19.76	4.88	42.70	52.42
8	13.49	55.42	30.85	8.68	38.22	53.09
9	13.91	52.46	33.84	10.86	37.24	51.90

3.7 The influence of coagulant dose and pH on species reduction

The species of PAC-PDMDAAC were varied in the coagulation process, which could help explain the coagulation mechanisms. With PAC-PDMDAAC, the species reduction rates were investigated by varying coagulant doses and the initial pH solution for treatment of the artificial lake. The results are shown in Figure 7.

Figure 7a shows the increase of species reduction rates with the increase of coagulant dose at an initial solution of pH 7. With a lower dose, the monomeric species reduction was generally lower than for the other species; thus, DON and DOC removal was dependent on reduced proportions of medium and colloidal species. Throughout the whole coagulant dose regime, the species reduction rates of medium and colloidal species was higher. Monomeric species reduction increased with the increased coagulant dose. The increased dose was not beneficial to the reduction in DON. Therefore, the main species determined DON removal was possible, not the monomeric species.

Figure 7b shows the variation of species with the increase of pH at a coagulant dose of 20 mg/L. With the increase of pH, the species reduction increased. Between at pH 4 and 5, the monomeric species reduction rate was higher than with other species. Therefore, the monomeric species had a more significant role at lower pH conditions, of which reduction mostly resulted from charge neutralization. At pH 6, the reduction rate of colloidal species began to increase over the reduction rate of monomeric species, which showed that floc sweeping began to react with pollutants to reduce organic matter. With the increase of pH, all of species decreased rapidly and

the role of floc sweeping was increased. At pH 8 and 9, the monomeric species and medium polymeric species were most completely reduced up to over 97%. Because of larger reduction in species, the charged negative $Al(OH)_3$ flocs were possible the primary products in coagulation process at higher pH conditions.

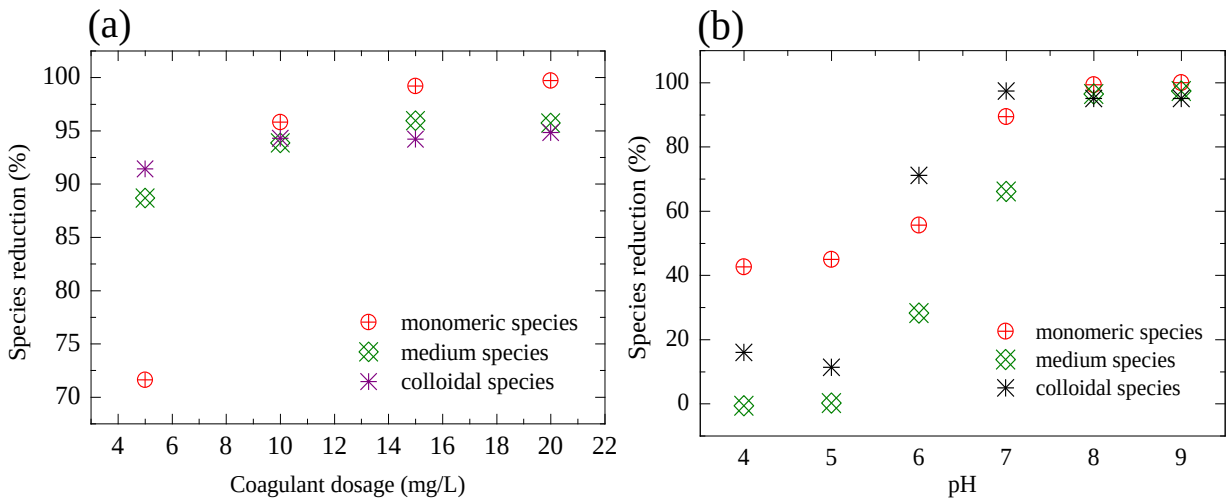


Figure 7 Species reduction rate percent by varying (a) coagulant dose and (b) pH with coagulant dose of 20mg/L. The test was performed on a sample that had not undergone restabilization.

3.8 Correlation analysis

The correlations of reduced coagulant species with turbidity and DOC removals were positive with the increase of coagulant dose. However, the correlations of reduced coagulant species with turbidity and DON removals were negative with the increase of coagulant dose as shown in Figure 8(a-c). At a lower coagulant dose, the flocculation for DOC and turbidity was not effective, and more adsorption sites for DON seemed possible. However, with the increase of coagulant dose, the DOC and turbidity reduction increased and most of adsorption sites were used to absorb DOC and turbidity. Less adsorption sites remained for DON, and its site amount was gradually

462 reduced with an increased coagulant dose. DON removal was, therefore, decreased resulting in a
463 negative correlation with reduced species. The correlations of reduced species with turbidity,
464 DOC and DON removals were all positive with the increase of pH as shown in Figure 8(d-e). At
465 pH 4-5, the turbidity and DOC removals were lower and coagulation was mainly dependent on
466 charge neutralization. At pH 6, the DOC and turbidity removals were higher than 60%. With
467 doses of pH 7-9, almost no significant changes occurred. More colloidal adsorption sites were
468 generated when the pH increase caused the removal of DON. A larger transformation of
469 monomeric species and medium species to colloidal species was beneficial to the growth of
470 adsorption sites thus enhancing DON removal. The positive correlation indicated that adsorption
471 site distribution affected pollutants removal.

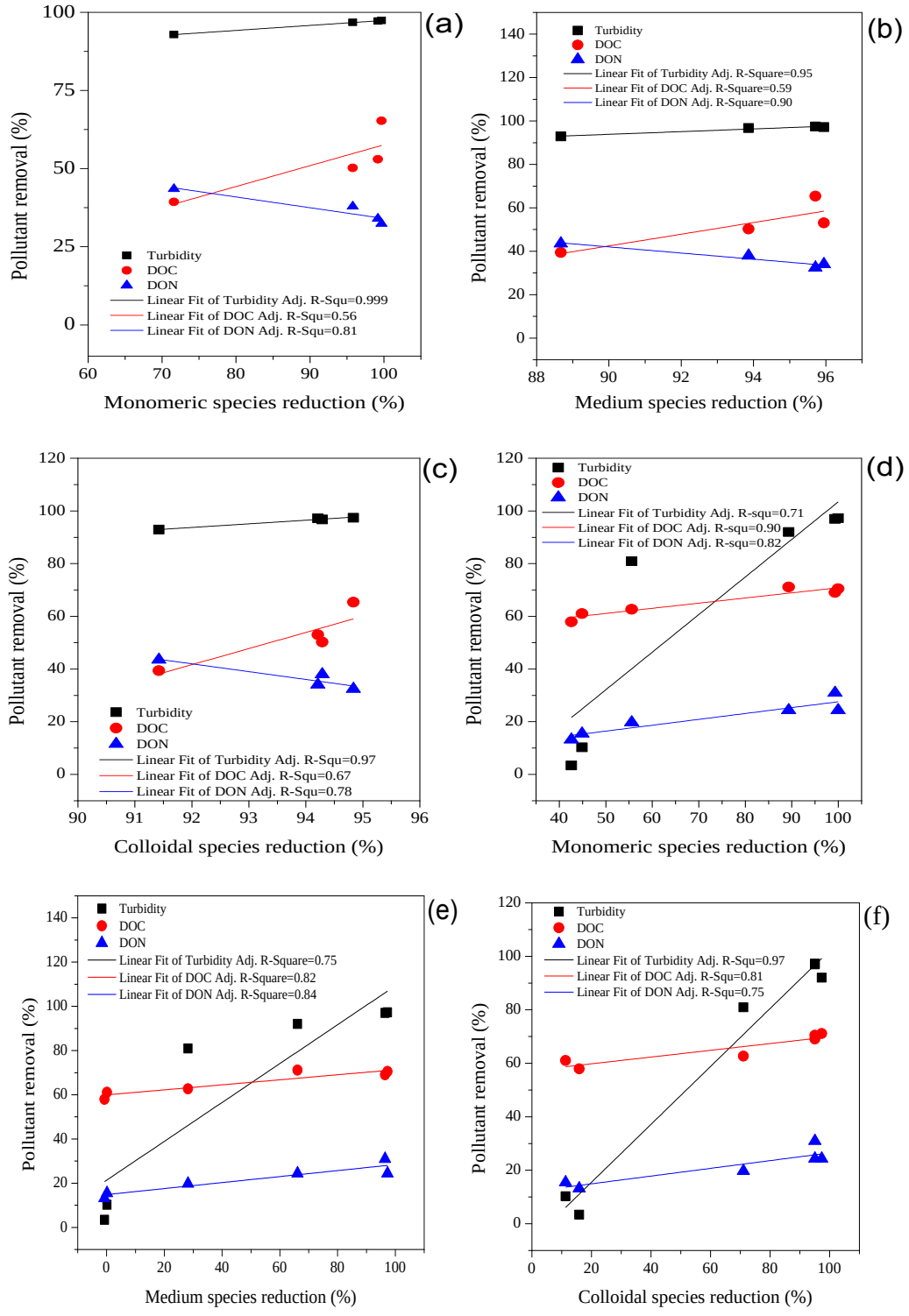


Figure 8 Correlation of species reductions with turbidity, DON and DOC removal rates. The data was collected from coagulant dose effect (a-c) and pH effect (d-e).

3.9 Applicability to other types of water source

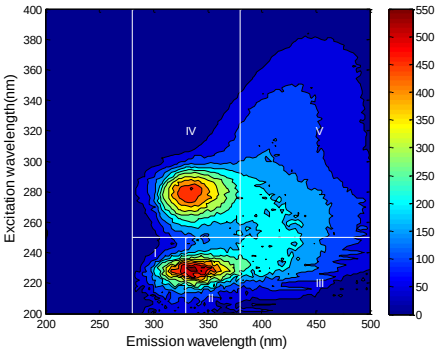
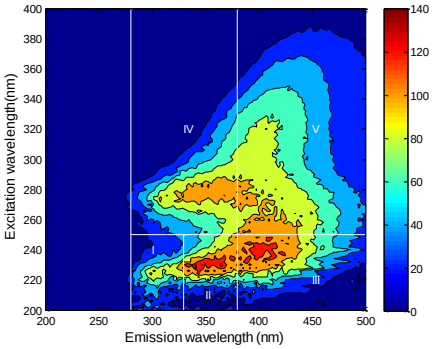
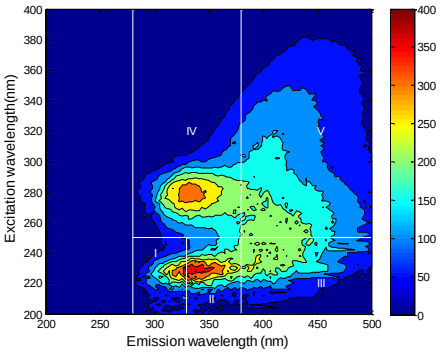
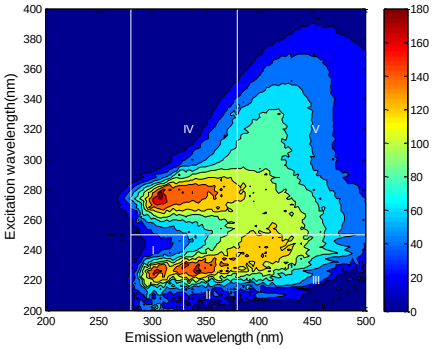
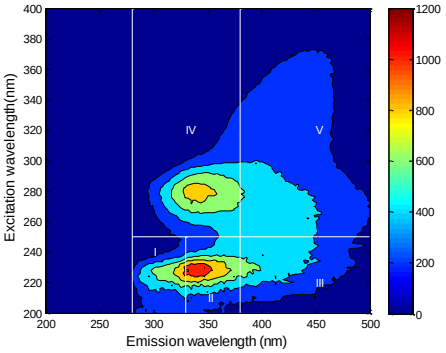
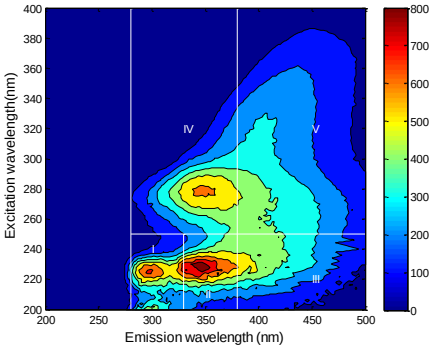
The PAC-PDMDAAC can be applied to other types of water source with higher species reduction. To obtain an optimum treatment of water, we used a predetermined coagulant dose to reach optimum turbidity removal. All coagulations were performed at pH 8.

Table 3 Applicability of PAC-PDMDAAC to different types of source water.

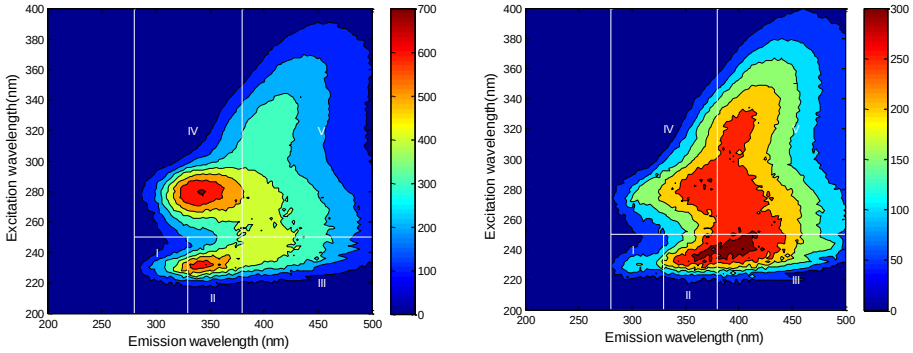
Water Type	Dose (mg/L)	Residual turbidity (NTU)	UV254 (%)	DOC (%)	DON (%)	Monomeric species (%)	Medium species (%)	Colloidal species (%)
Upstream River	16	0.25	62.34	60.86	24.33	97.00	96.24	97.26
Downstream River	16	0.23	60.61	58.60	23.97	97.00	95.79	98.30
Wetland water	24	0.29	65.68	60.56	34.41	93.46	98.03	99.39
Wastewater effluent	24	0.25	77.65	71.18	45.76	96.67	98.27	98.08
Artificial Pool water	24	1.13	74.60	70.02	28.68	93.99	98.73	96.01
Natural Pool water	20	0.23	74.29	67.61	21.07	93.74	94.21	91.82
Algal solution	16	0.21	68.12	62.77	25.15	93.21	94.66	91.59
Artificial lake water	20	0.25	75.86	71.61	30.89	99.34	96.47	95.10

Table 3 show that all species were almost completely removed. This indicates that PAC-PDMDAAC interacts well with the pollutants in a wider range of aquatic environments. The smallest DOC removal was reduced up to over 55% while the largest removal was up to 71.61%. The smallest DON removal was reduced by slightly more than 20% and the largest removal reached 45.76%. With the initial turbidity value at less than 10 NTU, the residual turbidity after

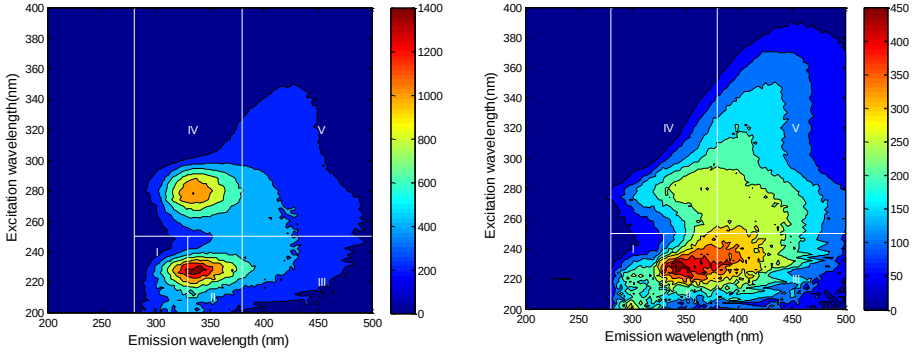
490 treatment was lower than 0.3 NTU. With the initial turbidity value higher than 70 NTU, the
491 residual turbidity of modeling humic acid suspension was up to 1.14 NTU. For treatment of pool
492 water with the initial turbidity value of 32.4 NTU, the residual turbidity could be reduced up to
493 1.13 NTU. An appropriate dose for turbidity removal does not imply a better removal of DON.
494 The doses that were required for better removal in turbidity and DOC were approximate and
495 DON removal was better with other specific coagulant doses.
496
497 ***3.10 Fluorescence assessment on removal of DON fractions***
498 In this study, we used fluorescence spectroscopy to assess DOM fractions composition and their
499 removals by calculating the FRI values of different DOM fractions. Table 4 shows the DOM
500 fractions with different source type. These results were obtained with coagulant dose optimized
501 by assessing turbidity reduction rate. From this table, the fluorescence intensities of spectra can
502 be seen to be decreased. The fractions reductions rates were shown in Table 5. It shows that
503 aromatic protein I, aromatic protein II and soluble microbial byproduct-like, the mean reduction
504 rate (56.47%) of soluble microbial byproduct-like was the highest. However, other two fractions
505 were reduced to a mean degree of 48.72%. The effectiveness of coagulation was varied for
506 different water sources. For example, for natural pool water it showed that the aromatic protein I
507 was the mostly reduced, followed by soluble microbial byproduct-like. The mean values of
508 carbon-based species DOM fractions that were fulvic acid-like and humic acid-like were 48.07%
509 and 50.66%, which showed the similar removal degrees to that of those nitrogen-based DOM
510 fractions species (aromatic protein I, aromatic protein II).
511
512 **Table 4** Spectra variations of DOM from different coagulation systems.

Source water	Raw water	After treatment
Upstream River water		
Downstream River water		
Wetland water		

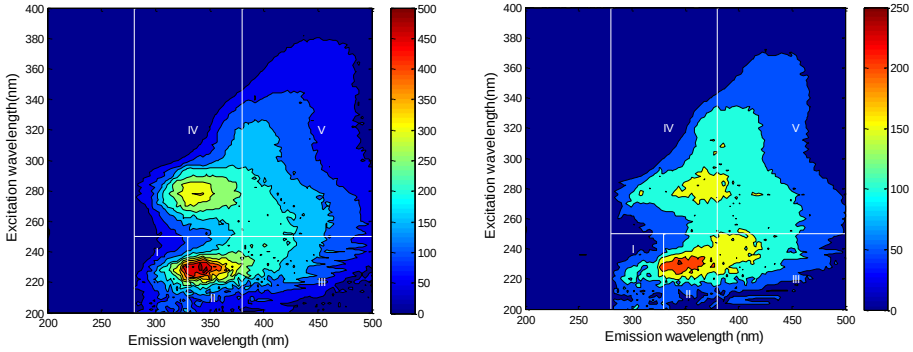
Wastewater plant effluent



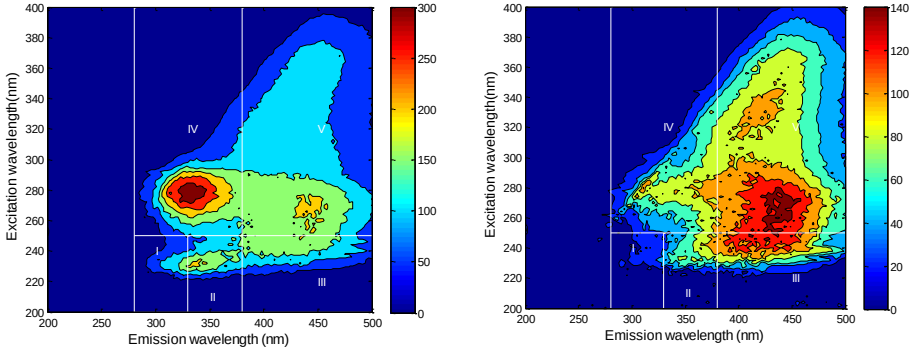
Artificial Pool water



Natural pool water

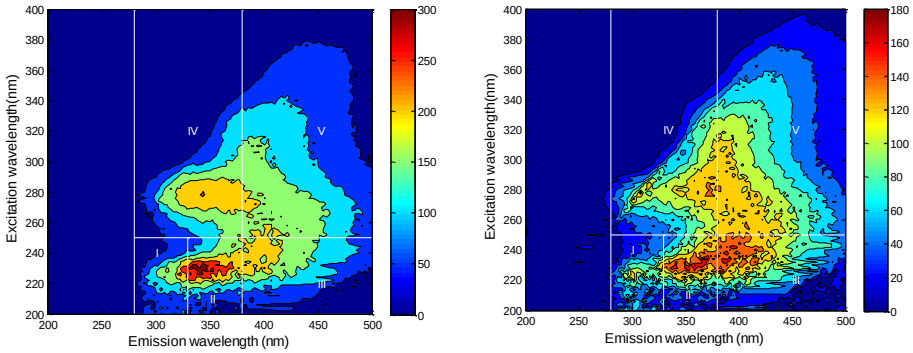


Algae solution



Artificial

lake water



513

514 **Table 5** DOM fractions reduction rates with different sources.

No	Aromatic protein I, (%)	Aromatic protein II (%)	Fulvic acid-like (%)	Soluble microbial byproduct-like (%)	Humic acid-like (%)
1	68.40	68.47	70.05	75.22	68.34
2	37.00	51.16	55.17	45.77	56.81
3	8.58	20.71	32.71	33.75	38.41
4	55.01	50.22	44.61	59.18	41.80
5	67.10	57.28	51.21	68.90	58.05
6	44.63	45.41	50.54	56.46	55.08
7	69.79	55.33	37.18	60.16	34.49
8	39.22	41.60	43.10	52.30	52.26
Mean	48.72	48.77	48.07	56.47	50.66

515

516 **4 CONCLUSIONS**

In this study, the enhanced removal behaviors of DON and DOC by PDMDAAC in Al-based coagulation with PAC were observed, and related mechanisms were revealed. With PAC-PDMDAAC, floc settling efficiency was significantly higher than that of PAC with a higher G_r value of 154.99 μm/min and R_f value of 16.27%, showing a better adsorption-bridging function and better recovery capacity after breakage. The cationic polymer increased the amount of colloidal species thereby reducing other species amount under different pH conditions, which required increased cationic polymer doses. The colloidal species might increase the adsorption-bridging and floc sweeping effects of DON and DOC. Because the amounts of medium species and monomeric species were decreased so the increase in charge neutralization capacity could be assigned to the introduction of a cationic charge from PDMDAAC. The dominant species in removal of DON and DOC were the colloidal species. The PAC-PDMDAAC presented higher removal efficiency than PAC. Coagulant dose and pH affected DOC and DON removal: better removal of DOC required a higher pH dose than that required for the removal of DON; the increased pH provided more adsorption sites for removal of DON. DON and DOC removal achieved the maximum at pH 8. All species were almost completely removed. The removal of DOC, DON and turbidity reduction were dependent on multiple interactions of charge neutralization, adsorption-bridging and flocs sweeping. Among them, DON and DOC removals were mainly dependent on adsorption bridging and floc sweeping; turbidity removal was determined by charge neutralization.

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REFERENCES

[1] J. I. Hedges, B. A. Bergamaschi, R. Benner, *Mar Chem*, **1993**, *41, 141*.

[2] Z. Li, C. Liu, Y. Dong, X. Chang, X. Nie, L. Liu, H. Xiao, Y. Lu, G. Zeng, *Soil Till Res* **2017**, *166, 1*.

[3] S. C. Bolyard, D. R. Reinhart, *Waste Manage* **2017**, *65, 47*.

[4] M. H. Lee, J. H. Park, E. Matzner, *Geoderma* **2018**, *310, 163*.

[5] G. Zhu, W. Qian, J. Yin, Z. Li, Z. Peng, B. Ren, G. Fan, W. Peng, *Water Res* **2016**, *100, 201*.

[6] S. Gur-Reznik, , I. Katz, , C.G. Dosoretz, *Water Res* **2008**, 42, 1595.

[7] A. D. Shah, W. A. Mitch, *Environ Sci Technol* **2011**, *46, 119*.

[8] E. Pehlivanoglu-Mantas, D. L. Sedlak, *Water Res* **2008**, *42, 3890*.

[9] W. Lee, P. Westerhoff, J. P. Croué, *Environ Sci Technol* **2007**, *41, 5485*.

[10] E. Bei, Y. Shu, S. Li, X. Liao, J. Wang, X. Zhang, C. Chen, S. Krasner, *Water Res* **2016**, *98, 168*.

[11] T. C. Ng, H. Y. Ng, *Water Res* **2010**, *44, 2336*.

[12] Z.X. Luo, Q.S Wei, Z.H Wang, C.Y. Yan, *Ecol Environ Sci* **2010**, *19, 45*.

[13] K. Czerwionka, *Oceanologia* **2016**, *58, 39*.

[14] A. Aryal, *Desalin. Water Treat* **2016**, *57, 13608*.

[15] M. Tomaszewska, S. Mozia, *Water Res* **2002**, *36, 4137*.

[16] Y. Deng, R. Zhao, Curr Pollut *Rep* **2015**, *1, 33*.

[17] L. B. Guldberg, *Limnol Oceanogr* **2015**, *47, 1712*.

[18] J. Zhang, M. Su, B. Xi, G. Qian, J. Liu, F. Hua, S. Huo, *J Environ Sci-China* **2016**, *50, 56.*

[19] D.L. Sedlak, J. Jeong, H. Liu, "Uptake by Algae of Dissolved Organic Nitrogen from BNR Treatment Plant Effluents" in executive summary , Iwa Publishing, Alexandria VA 2013, p. 1-2.

[20] B. Liu, L. Gu, X. Yu, G. Yu, H. Zhang, J. Xu, *Sci Total Environ* **2012**, *414, 508*.

[21] J. Liao, Y. Y. Liu, X. M. Chen, *Water Sci Eng Technol* **2010,** *1, 33*.

[22] H. Liu, *Environ Sci Technol* **2012**, *46, 713*.

[23] H. Hu, L. Ding, J. Geng, H. Huang, K. Xu, H. Ren, *J Enviro Chem Eng* **2016**, *4, 2536*.

[24] W. Lee, P. Westerhoff, *Water Res* **2006**, *40, 3767*.

[25] B. Liu, L. Gu, X. Yu, H. Zhang, *Aqua* **2012**, *61, 41*.

[26] A. Matilainen, M. Vepsalainen, M. Sillanpaa, *Adv Colloid Interfa* **2010**, *159, 189*.

[27] R. B. Gustafson, Evaluation of enhanced coagulation for the removal of dissolved organic nitrogen and the control of nitrogenous disinfection byproduct formation, Master thesis, University of North Carolina, Ann Arbor 2012, p. *i*.

[28] C. Liu, S. He, B. Wang, J. Wang, W. Chen, *Water SCI Tech-WS* **2016**, *16, 1432*.

[29] B. Liu, G. Z. Yu, L. Gu, C. M. Zhao, Q. F. Li, H. M. Zhai, *Environ SCI* **2013**, *34, 1392*.

[30] M. T. Orta de Velásquez , A. E. Campos-Reales-Pineda , I. Monje-Ramirez , I. Yáñez Noguez, *Ozone-SCI Eng* **2010**, *32, 323*.

[31] P.K. Jin, Y.Y Zhang, Y.N Feng, X.C Wang, *Acta Sci Circum* **2013**, *33, 1553*.

[32] W. Lee, P. Westerhoff, *Water Res* **2006**, *40, 3767*.

[33] G. Li, L. Bing, Y. Xin, *Science Bulletin* **2010**, *55, 3098*.

[34] M. Bahram, R. Bro, C. Stedmon, A. Afkhami, *J Chemometr* **2006**, *20, 99*.

[35] W. Chen, P. Westerhoff, J. A. Leenheer, K. Booksh, *Environ Sci Technol* **2003**, *37, 5701*.

[36] B. Tian, *Environ Chem* **1989**, *8, 27*.

[37] Peter Jarvis, Bruce Jefferson, Simon A. Parsons, Breakage, Regrowth, and Fractal Nature of Natural Organic Matter Flocs, *Environ Sci Technol* **2005**, 39, 2307.

[38] S. Sadri Moghaddam, M. Alavi Moghaddam, M. Arami, *J Environ Manage* **2011**, *92, 1284*.

[39] R. Subramanian, S. Zhu, R. Pelton, *Colloid Polym Sci* **1999**, *277, 939*.

[40] P. C. Wen, *Chemosphere* **2002**, *47, 963*.

[41] X. Bo, B. Gao, N. Peng, Y. Wang, Q. Yue, Y. Zhao, *Chem Eng J* **2011**, *173, 400*.

[42] S. B. M. Boller, *Water Sci Technol* **1998**, *37, 9*.

[43] Q. Chang, Fu, J.Y., Li, Z.L., "*Principles of Flocculation", Lanzhou University Press*, 2rd edition, Lanzhou **2001, p. 1-258**.

[44] Z. Yang, B. Liu, B. Gao, Y. Wang, Q. Yue, *Sep Sci Technol* **2013**, *111, 119*.

[45] M. Sadrnourmohamadi, B. Gorczyca, *Sep Sci Technol* **2015**, *50, 2075*.

[46] M. Yan, D. Wang, J. Qu, W. He, C. W. K. Chow, *J Colloid Interf Sci* **2007**, *316, 482*.